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## COMPLETE SPECIFICATION

## Synthetic Elastomers and their preparation

We, ESPE FABRIK PHARMAZEUTISCHER PRÄPARATE GMBH, a German Body Corporate of Seefeld/Oberayern, Germany, do hereby declare the invention for which we pray that

5 a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to polymers containing ethylene amine groups, their preparation and the production of synthetic elastomers from such polymers.

15 Rubber-like products are generally made by the polymerization of unsaturated hydrocarbons with one or more olefinic double bonds. having rubber-like properties is the thioplasts which are the known reaction products of aqueous solutions of alkali metal polysulphides with aliphatic dihalides.

20 Other known synthetic rubbers are the silicone rubbers and polyurethanes.

The known synthetic rubbers, however, have the disadvantage that their processes of preparation are comparatively complicated or, as in the case of the silicone rubbers, are expensive and yield products having unsatisfactory mechanical properties, at least when made without fillers. The thioplasts exhibit an unpleasant odour before crosslinking, the odour being partly present even after vulcanization. The polyurethane preliminary products cannot be stored for long periods, since they still contain isocyanate. In addition, they present physiological dangers, and also they need very careful handling with exclusion of water. When using so-called "blocked" diisocyanates, these disadvantages are lessened, but rather high temperatures have to be used in the operation.

40 The particular properties and typical uses

of these known rubber materials are given in Ullmann "Encyclopaedie der technischen Chemie," third edition, volume 9, pages 346 to 350.

It is also known to produce coatings and shaped bodies from polymerization products of ethylene imine or its derivatives. Finally, German Specification 1,020,790 describes a process for making crosslinked polyester resins in which ethylene imine is added to certain unsaturated polyesters. The resultant products have a comparatively low ethylene imine equivalent and can be converted into fairly hard products. The term "ethylene imine equivalent" denotes the amount of the substance in grams containing 1 mol ethylene imine groups.

It has been found unexpectedly that polymeric substances containing comparatively few ethylene imine groups, that is to say, in which the reactive groups are present as it were in a rather diluted state, can be polymerized to yield transparent rubbery products having permanent elasticity and having properties which make them readily applicable to a great variety of technical applications. This is surprising since the crosslinked ethylene imine derivatives described in publications are hard or brittle substances in which high mechanical strength, e.g. great hardness, is emphasized as particularly desirable.

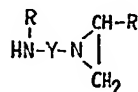
In one aspect, therefore, the present invention provides a process for the preparation of synthetic elastomers which comprises crosslinking a substantially linear polymer which contains on average more than one ethylene imine group per molecule, and which has a mean molecular weight of at least 1,000 and an ethylene imine equivalent of at least 500.

The invention also provides modified poly-

mers suitable for the formation of synthetic elastomers which are substantially linear polyesters, polyethers or polythioethers containing on average more than one ethylene imine group per molecule, preferably 1 to 5 groups with 1.8 to 2.5 groups per molecule being especially preferred, and having a mean molecular weight of at least 1,000, preferably between 3,000 and 25,000 and more especially between 6,000 and 15,000, and an ethylene imine equivalent of at least 500, preferably 1,000 to 8,000. Advantageously these modified polymers should have a viscosity not greater than 30,000 poises at 70° C., preferably between 1 and 30,000 poises at 25° C. and more especially 10 and 10,000 poises at 25° C. These figures refer to the viscosity of the substances actually used, or their solutions, without the addition of fillers.

Substances of molecular weight above 20,000, and substances which tend to crystallise at room temperature are preferably processed at higher temperatures or in admixture with low molecular weight polymers.

In a further aspect the invention provides processes for the preparation of the above-mentioned modified polymers. In one such process a polyester, polyether or polythioether containing carboxyl groups or amide-forming derivatives thereof is reacted with an ethylene imine derivative of the formula:

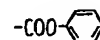


wherein R represents a hydrogen atom or an alkyl group and Y represents a bivalent organic radical. In another process a polyester, polyether or polythioether containing hydroxyl groups is reacted with a difunctional intermediate compound in which one function will react with a hydroxyl group and the other with a hydroxyl group and/or an amino group, and the resultant derivative is reacted with ethylene imine or an ethylene imine substituted amine or alcohol. Suitable difunctional intermediates or unsaturated carboxylic acids, diisocyanates, and halogen substituted carboxylic acids. Alternatively ethylene imine or an ethylene imine substituted amine or alcohol may be reacted with a starting material of a polyester or polyether containing within the chain or attached thereto groups which will react directly with the ethylene imine compound.

In another aspect the invention provides a process for the preparation of synthetic elastomers which comprises crosslinking a modified polymer as hereinbefore described by means of a crosslinking agent.

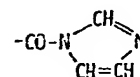
As a general rule the synthetic elastomers made according to this invention have properties similar to hard rubber when the starting materials used are at the lower limit of the above-mentioned ranges of molecular and equivalent weights. They possess frequently a somewhat lower tear resistance, at least when they are unfilled.

When the starting polymer contains carboxyl groups or amide-forming derivatives thereof, these derivatives may be esters which are easily converted into acid amides by aminolysis, e.g. methyl esters, and so-called "activated esters," e.g. aryl esters of the general formula:



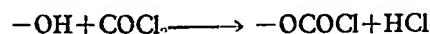
Particularly useful "activated esters" are the aryl esters with negative substituents on the benzene ring, such as nitro groups or halogen atoms. Examples are the 3,5-dichlorophenyl ester, 2,4-dichlorophenyl ester, 2,4-dibromophenyl ester, 4-nitrophenyl ester, 2,4,5-trichlorophenyl ester, and 2,4-dinitrophenyl ester.

The N-acyl compounds of the polymers which are very active are likewise suitable. By these are meant acid amide groupings which are easily split by aminolysis, for instance imidazolides of carboxylic acids of the general formula:



As a rule it is not necessary to isolate the derivatives which can be aminolysed particularly easily and under mild conditions; thus, the activated ester or the N-acyl compound capable of aminolysis can be prepared and immediately thereafter reacted with an alkylene imino derivative whereby the ethylene imine groups are introduced into the macromolecules with formation of acid amide bonds.

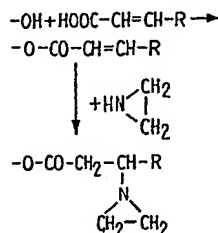
Among other useful carboxyl derivatives are also carboxylic chlorides, which term is used herein to include carbonic ester chlorides (which are also known as chloro-formic acid esters or chlorocarbonic acid esters) which are most conveniently obtained by reaction of phosgene with OH groups according to the equation:



The most suitable starting materials are those polyesters or polyethers in which the

hydroxyl and/or carboxyl groups are predominantly in terminal positions, since these have the advantage that they lead to elastomers with more uniform chain lengths between the crosslinking points and have, therefore, superior mechanical properties.

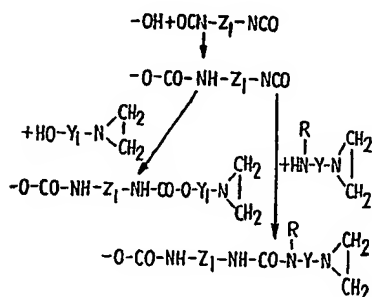
When a hydroxy containing starting material is reacted with an  $\alpha,\beta$ -unsaturated carboxylic acid the reaction may be represented as follows:



Preferably the  $\alpha,\beta$ -unsaturated carboxylic acid is crotonic or acrylic acid.

Suitable halogen substituted carboxylic acids for reaction with hydroxyl-containing starting materials are chloro acetic acid and  $\alpha$ -bromo-butyric acid. The acylation can be carried out in different ways, e.g. by esterification in the presence of an acid catalyst by means of acid anhydrides or acid chlorides. Suitable diisocyanates are: 2,4-tolylene-diisocyanate, 4,4'-diphenylmethane-diisocyanate, naphthalene-1,5-diisocyanate, hexane-1,6-diisocyanate. In the diisocyanate addition it is frequently advisable to work at low temperatures in order to avoid side reactions, though this can be achieved by the use of highly active catalysts, such as tertiary amines, or metal compounds, e.g. zinc acetyl-acetonate or organotin compounds. In general, these catalysts do not disturb the subsequent processing of the substances. Also useful are the so-called "isocyanate-lengthened" polyesters having urethane groups in the chain.

The reaction of hydroxyl-containing starting materials with diisocyanates and their subsequent reaction with ethylene imine derivatives containing OH- or amino groups is illustrated by the following reaction scheme:



wherein  $Z_1$ , Y and  $Y_1$  are bivalent organic radicals,

$Z_1$  is preferably an alkylene group or a bivalent aromatic radical,

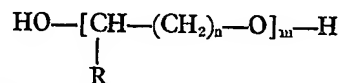
Y and  $Y_1$  are preferably alkylene groups which may be interrupted by ether- or acid-amide groups, and

R=H or alkyl.

Compounds containing carboxyl substituents may be reacted in a similar manner.

Suitable polyether starting materials are polymers and copolymers of cyclic ethers, especially with 3 to 5 ring members, such as ethylene oxide, propylene oxide, tetrahydrofuran, oxetane (trimethylene oxide), and substitution products thereof. Products having a limited degree of branching are also useful, e.g. those derived from starting materials containing minor amounts of polyoxyalkylation products of tri- or higher polyhydric alcohols.

The polyethers best suited to the present process are those of the following formula:



wherein  $n=1, 2$ , or  $3$ ,

$m$ =the mean polymerization degree, preferably about 25 to 500, and

R=H or alkyl.

In copolymer, R may have different meanings in the same molecule.

If the starting materials do not already contain carboxylic groups as substituents, these may be introduced by known means, for example by the reaction of terminal or lateral hydroxyl groups with isocyanate carboxylic esters (*N*-carbonyl-amino-acid esters). These may be isocyanato acetic acid ester,  $\alpha$ -isocyanato propionic esters, 6-isocyanato caproic ester, 11-isocyanato undecanoic ester. Furthermore, polymers with terminal or lateral OH groups, particularly polyethers, may be provided with carboxyl groups by reaction with dicarboxylic acid or their derivatives, e.g. succinic acid or phthalic acid or their anhydrides.

Another possibility is the conversion of terminal or lateral hydroxyl groups (the latter being, for instance obtainable by incorporation of glycidic acetate into a polyether, and subsequent saponification) with phosgene into chloro-formic acid esters and to react them thereafter with amino acid esters. If, in this reaction, esters of secondary amino acids are used, urethane esters are obtained which contain an *N*-alkyl group in the urethane radical instead of an NH group. The chloro-formic acid ester may also be reacted with alkylene imino amines directly as described earlier.

So-called isocyanate-lengthened polyethers are also useful, i.e. comparatively low molecular polyether glycols whose molecular weight is increased by reaction with polyvalent iso-

cyanates. As a rule, diisocyanates are preferably used for the purpose, since the products should substantially be of linear structure.

Moreover, it is possible to incorporate cyclic ethers with carboxylic groups, preferably epoxides (e.g. epoxidized olefinic carboxylic esters such as 4,5-epoxy-valericmethyl ester, or 10,11-epoxy-undecanoic ethyl ester), into polyethers by copolymerization. Esters of glycidic acid are less suitable, since they often yield unstable polymers.

Wherever it is desired to prepare an elastomer having a high stability to hydrolysis from the modified polymers, polyethers are the preferred material.

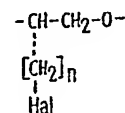
The polyesters best suited for the present invention are those derived from dicarboxylic acids and diols. Suitable acids and diols are as follows: acids; succinic, glutaric, adipic, pimelic, azelaic, sebacic,  $\alpha,\alpha$ -dimethyladipic, phthalic, terephthalic, *p*-phenylene-diacetic, dicarboxylic acids containing ether and thioether groups, e.g. 2,5-dioxahexane-dicarboxylic acid-1,6; 2,2'-ethylenedithio-diocetic acid, 2,2'-*p*-xylylenedithio-diacetic acid; and glycols; ethylene-glycol, propanediol-1,2, propanediol-1,3, butanediol-1,3, hexanediol-1,6; 2-ethylhexanediol-1,3; 2,2-dimethylpropanediol-1,3; 2-methyl-2-propyl-propanediol-1,3, triethyleneglycol, tripropylene-glycol, polyethyleneglycols, polypropyleneglycols and triethyleneglycol. Benzene derivatives should preferably be used in comparatively small amounts in mixture with aliphatic dicarboxylic acids or diols.

The simultaneous use of small amounts of tri- or tetra-functional alcohols, such as trimethylol propane or pentaerythritol or carboxylic acids, e.g. tricarballic acid, is possible and in some cases even advantageous for the final products. It is sometimes advisable to use polyesters with carboxylic terminal groups which may be prepared from polyesters having terminal OH groups by a reaction similar to that described above for polyethers. As a rule, the groups used in preparing the polyesters will be so chosen that the latter will have comparatively low melting points in order to suppress tendencies for crystallization in the elastomers. This can be done in known manner, e.g. by using groups with an odd number of chain members or by incorporation of ether groups. In a similar manner, the hydrophilic character of the end products can be influenced largely by the selection of the starting materials, e.g. propylene oxide products are highly hydrophilic, whereas the incorporation of dicarboxylic acids or diols obtained from di- or poly-siloxanes into polyesters, gives elastomers which are hydrophobic. Suitable di- and poly-siloxanes are: bis-3,3'-carboxypropyl-tetramethyl-disiloxane; bis-4,4'-carboxybutyl-tetramethyl-disiloxane; bis-3,3'-carboxypropyl-octamethyl-tetrasiloxane and bis-oxy-methyl-tetramethyl-disiloxane.

Other polyethers which may be used are polythioethers or poly-ethers containing thioether groups, which may be obtained by polycondensation of thiodiglycol. Linear polyacetals are also suitable, though they will, of course, have to contain terminal or lateral OH or carboxylic groups, or will have to be provided therewith in a known manner.

As indicated above, the starting material may be a polyester or polyether containing groups or substituents in the chain or attached thereto which can react with ethylene imine, for example polyesters derived from  $\alpha,\beta$ -unsaturated dicarboxylic acids, e.g. fumaric acid or halogen dicarboxylic acids, e.g.,  $\alpha,\alpha$ -dibromoadipic acid. Especially useful polyesters are mixed condensates which contain, in addition to saturated dicarboxylic acids, a certain amount of maleic acid or itaconic acid, to which ethylene imine may be added in a known manner.

Suitable polyethers are those into which a certain amount of halogen substituted epoxides, e.g. epibromohydrin, are incorporated by polymerization. These substances contain units with short halogen-substituted side chains:



(*n* being preferably 1—4). Examples of such compounds are polymers or copolymers of ethylene oxide, propylene oxide or tetrahydrofuran of mean molecular weight 2,000 to 20,000 with at least 2, preferably 3 to 10, halogen-substituted side chains.

Instead of halogen-substituted epoxides, it is possible to incorporate by polymerization epoxides containing  $\alpha,\beta$ -unsaturated carboxylic acid residues. Particularly useful is glycidic acrylate or glycidic crotonate. By copolymerization with cyclic ethers, polyethers are obtained having activated double bonds in the side chains. Furthermore, copolymers of cyclic ethers with other esters of epoxy alcohols, e.g. glycidic acetate, can be used as starting material. From these, polyglycol ethers may be obtained by saponification having OH groups in the side chains.

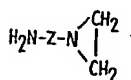
All the above-mentioned types of polyglycol ethers with substituted side chains may be modified by reacting them directly with ethylene imine, or by first introducing some substituents which are, in turn, capable of reacting with suitable ethylene imine derivatives. Thus, in the above-mentioned halogen-containing polyethers the halogen atoms can be exchanged with ethylene imine directly, or they are preferably first converted into amino groups by means of excess ammonia or potassium phthalimide, said amino groups being thereafter reacted with ethylene imine carboxy-

lic acid esters. Since the halogen-containing polyethers act as alkylating agents and might therefore initiate undesired crosslinking reactions, care should be taken that the halogen atoms are substituted as far as possible, e.g. by amino groups, or that residual halogen should be eliminated by treatment with alkali metal alcoholate.

Similar considerations apply to polyethers whose terminal OH groups are substituted by halogen; these too may be exchanged with amino groups which may then be reacted, e.g. with ethylene imine carboxylic esters.

To polyethers having activated double bonds in the side chains, e.g. those obtained from glycidic crotonate, ethylene imine may be directly added. Finally, polyethers with terminal OH groups and/or OH groups in the side chains may be provided with ethylene imine groups according to the above-described methods, preferably by acylation with suitable carboxylic acids or reaction with at least bi-functional isocyanates, and subsequent reaction with ethylene imine or its derivatives.

Any ethylene imine derivative containing at least one primary or secondary amino group in the molecule may be used, though those with primary amino groups have the advantage of smooth reaction. They are represented by the formula:



wherein Z stands for a bivalent organic radical. When using secondary amines, it is generally necessary to convert the carboxylic groups first into easily aminolysable groups, e.g. into a cyanomethyl ester.

A preferred class of ethylene imine derivatives are those of the formula:



wherein R=H or alkyl. Particularly useful are e.g. 2-ethyleneimino-ethylamine, 3-ethyleneimino-propylamine, 3-ethyleneimino-butylamine, 5-ethyleneimino-pentylamine, 7-ethyleneimino-heptylamine.

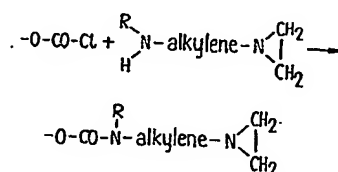
The alkylene chain may be interrupted by other groups, e.g. ether or acid amide groups. The latter type of substances in which an ethylene imino carboxylic acid is linked to a diamine in the manner of an acid amide may be obtained, for example, by reaction of ethylene imino carboxylic esters with diamines. Among these compounds are  $\alpha$ -ethylene-imino-

carboxylic acid derivatives which have the advantage of particularly low basic character.

Where a hydroxyl-containing ethylene imine derivative is required the preferred compound is 3-ethylene imine propanol-1.

There are several methods for introducing the alkylene imino groups into the above-mentioned polymers with formation of acid amide groups.

In principle, all methods known for the formation of amide and peptide bonds may be used provided that the ethylene imine group, which is known to be liable to reaction and is likely to be attacked by acids and alkylating agents, is not attacked. The term "amide bonds" includes the amides of carbonic acid half-esters (carbamates) which are formed from carbonic acid ester chlorides by reaction with amines according to the following equation:



R=H or alkyl; and the alkylene group may be interrupted by suitable groups, e.g. ether or acid amide groups.

One such method for the formation of these amide and peptide bonds is the aminolysis of ester groups, especially methyl esters, preferably with addition of the conventional neutral or basic catalysts, such as diols, alcoholates, and the like. As mentioned before, a very advantageous modification of the process consists of using the aminolysis of "activated" esters, a large number of which have been described in the literature. The activated ester may, for instance, be obtained in a smooth reaction by conversion of carboxyl groups, containing polymers with diaryl carbonates, diaryl sulphites, or triaryl phosphites, e.g. bis-2,4-dinitrophenyl carbonate, bis-*p*-nitrophenyl sulphite or tris-2,4,5-trichlorophenyl phosphite they may be subjected to aminolysis by amino alkylene imines without isolation.

Other methods are those in which acid bonds are produced from carboxylic acids and amines by interaction of certain reagents with formation of active carboxyl derivatives as intermediates, as a rule so-called effective *N*-acyl bonds. Such reagents include *N*-carbonyl compounds of certain heterocycles, e.g. *N,N'*-carbonyl-diimidazol or carbodiimides, e.g. dicyclohexyl-carbodiimide, or *N*-cyclohexyl-*N'*-3-dimethylaminopropyl-carbodiimide.

Another such method is the reaction of acid chlorides with ethylene imino amines. Particularly suitable are the known carbonic acid ester chlorides (chloro-formic acid esters) of long chain diols (see equation I). In this

method chloro-formic acid esters can either be directly reacted with ethylene imino derivatives of primary or secondary amines, or can be converted into mixed carbonates by reaction with phenols in the presence of acid-binding agents, the mixed carbonates being, in turn, reacted with ethylene imine derivatives.

In all these processes, care has to be taken that acids or acid groups, including phenols, present or formed during the reaction, are neutralized or eliminated. This can be done by alkaline agents, such as NaOH, KOH,  $K_2CO_3$ , or preferably tertiary amines, e.g. triethylamine, which should be present in an excess amount; or by ion exchangers having basic groups. Especial care should be taken to remove Lewis acids if these are present, especially compounds of boron and particularly  $BF_3$  which are used for the polymerization of cyclic ethers, before ethylene imine or its derivatives are reacted. Such known operations, which are conventional in the stabilization of ethylene imine derivatives, will not be particularly set forth in the Examples.

As a rule, particularly when working with highly viscous starting materials, the use of a solvent is advisable. Such solvents are primarily inert liquids. The reaction temperature should not be above  $100^\circ C$ . in order not to affect the ethylene imine groups, the preferred range of temperature being between  $10^\circ C$ . and  $60^\circ C$ .

It is, of course, not necessary to provide every one of the carboxyl groups present in the polymer starting material with ethylene imine groups, thus it may be sufficient to react a polyester containing a mean amount of 8 carboxylic ester groups with sufficient ethylene imine amine to react with 3 to 4 of these groups.

As a general rule it should be noted that, in selecting the starting materials and the reaction conditions, care should be taken that groups capable of alkylation should not be present, or, if formed during the reaction, only in a manner capable of control, since they might be a disturbing agent during the subsequent crosslinking which is preferably initiated by alkylating agents. By groups capable of alkylation is mean primarily amino-, mercapto- and hydroxyl groups.

As crosslinking agents, the known alkylating agents and acids are useful, including Lewis acids; thus in principle all compounds which are capable of converting ethylene imine groups into ethylene immonium groups (see, e.g., German Patents Nos. 888,170 and 914,325).

Particularly useful are esters of strong acids e.g. sulphonic acid esters. The activity of such esters can be varied within wide limits by the choice of the alcohol component and, where derivatives of aromatic sulphonic acid esters are used, by variation of the substituents in

the benzene nucleus. When using sulphonic acid methyl esters at room temperature the crosslinking generally commences after several minutes and is practically complete after 20 to 50 minutes. On the other hand, isopropyl esters are extremely slow-acting crosslinking agents, the crosslinking often taking hours or days, even with higher temperatures.

Where it is desired to obtain especially high grade rubber qualities, it may be advisable first to mix the ethylene imine compound at room temperature with the crosslinking agents and then to heat, for some time, to slightly raised temperature, say  $50^\circ$  to  $100^\circ C$ .

If an extremely rapid crosslinking at room temperature or lower temperature is desired, aromatic sulphonic acid methylesters with negative substituents in the benzene nucleus may be used, e.g. halogen- or nitro-derivatives. Especially useful is the methylester of 2,5-dichlorobenzene-sulphonic acid.

Also useful are dialkyl sulphates, the activity of which is strongly dependent on the alcohol component. Thus, dimethyl sulphate is highly active. Mixed sulphates, e.g. methyl-lauryl sulphate are often useful.

Suitable crosslinking agents are sulphonic acids such as methane sulphonic acid, and phosphoric acid. Long-chain sulphonic acids, such as tetrapropylene benzene sulphonic acid, have the advantage of good solubility so that they can be readily incorporated into the polymer. Other organic acids may also be useful, particularly when mixed with alkylating agents. Lewis acids, such as borofluorides, are also useful, particularly in the form of complex compounds, e.g. with acid amides, such as *N,N*-dimethylacetamide.

Further examples of specific agents suitable for the crosslinking of the modified polymers of the present invention are: diethylsulphate, dipropylsulphate, asymmetric dialkylsulphate such as methylbutylsulphate, methane-sulphonic acid-methylester, methanesulphonic acid-allylester, methanesulphonic acid-butylester, ethanesulphonic acid-methylester; benzenesulphonic acid-methylester, benzenesulphonic acid-ethylester, benzenesulphonic acid-allylester, benzenesulphonic acid-isopropylester, *p*-toluenesulphonic acid-methylester, *o*-toluenesulphonic acid-methylester, *p*-chlorobenzenesulphonic acid-ethylester, 2,5-dichlorobenzenesulphonic acid-ethylester, *p*-nitrobenzenesulphonic acid-methylester, *p*-nitrobenzenesulphonic acid-isopropylester, *o*-chloro-*p*-nitrobenzenesulphonic acid-butylester, *p*-methoxybenzenesulphonic acid-methylester, *p*-ethoxybenzene-sulphonic acid-ethylester, naphthalene-1-sulphonic acid-ethylester, benzene-sulphonic acid, borofluoride-diethyletherate, borofluoride-dibutyletherate, borofluoride-tetrahydrofuran, borofluoride-butylacetate, tetrachloride; oxonium salts such as triethyl-oxonium-fluoborate, dimethyl-ethyl-oxonium-

fluoroborate triethyl - hexachloroantimoniate, and sulphonium salts such as triethylsulphonium-fluoborate.

When the crosslinking agents are solid at room temperature, they have to be used above their melting points or in the form of a solution, e.g. in a liquid crosslinking agent or in an inert solvent, such as diethylene glycol-dimethyl ether, dioxane, and benzene.

As a general rule, when alkylating agents are used as crosslinking agents they act more slowly or at a higher temperature as the alkyl radical contained therein becomes larger and more branched. Acids are particularly useful in mixture with alkylating agents. The crosslinking rate is, of course, not only dependent on the activity of the crosslinking agent, but also on the concentration of the ethylene imine groups in the preliminary products, and on the steric conditions as the ethylene imine groups and the neighbouring substituents.

If it is desired to slow down the rate of crosslinking to obtain a longer lasting pot-time, it may be necessary to use retarding agents. For this purpose, alkaline agents are suitable, especially those which are soluble in the ethylene imine derivatives. Suitable agents are alcohols of higher alcohols, and particularly tertiary amines. Amines of low volatility are generally preferred.

Since, as mentioned above, crosslinking is initiated by acids or alkylating agents, basic agents are useful as stabilizers against unintentional crosslinking, amines being preferred. When making the preliminary products care should also be taken, when ethylene imine or its derivatives take part in the reaction, that any acid groups which may be present, e.g. residual carboxylic groups in polyesters, are neutralized by basic agents.

The crosslinking and hardening agents are mostly liquids of low viscosity which are sometimes difficult to incorporate evenly into the more or less viscous masses. In order to overcome this difficulty, the hardening agents may be converted into a more viscous state corresponding to that of the polymer to be crosslinked. This may be done, for example, by the addition of a plastic, such as polyvinyl acetate, or by incorporating a filler with a large surface, such as highly dispersed silica.

Sometimes the use of solutions of the crosslinking agents in suitable softeners is advisable. In this manner it is not only possible to avoid undesirable mixing conditions, but it may be possible to provide easy incorporation into the ethylene imine polymers of crosslinking agents which are solid at room temperature, such as *p*-chlorobenzene-sulphonic acid-methylester.

It may be useful when dealing with crosslinking agents of moderate activity, such as *p*-toluenesulphonic acid-methylester which has a slow reaction time at room temperature, first to mix it into the ethylene imine compound in the cold, and subsequently to heat

the mixture to higher temperatures of about 50° to 100° C. This process is particularly useful when making large shaped pieces.

The crosslinking agent is usually added in an amount of 0.2 to 10% by weight, preferably 0.2 to 3%.

Unless it is desired to make use of the transparency of the elastomers made in accordance with this invention in making glass-like shaped articles or coatings, conventional fillers may be added to improve the mechanical properties, e.g. silica; silicates such as calcium silicate, zinc oxide, calcium carbonate, barium sulphate, quartz powder, barytes, fluorspar, calcium phosphate, and clay, as well as inorganic pigments or soluble dyes and disinfectants.

Since hardening may also be accomplished by the addition of acids, fillers having acidic reaction are, in general, not suitable since they lead to an uncontrollable hardening. Plasticizers are frequently compatible with ethylene imine derivatives and their use is not only advisable for economical reasons, but also for the improvement of other properties, especially the avoidance or reduction of crystallization. Among the useful plasticizers are phthalates, glycol derivatives, and polymer plasticizers. Finally, the simultaneous use of other ethylene imine derivatives, including low molecular weight ones, is possible in small quantities. In general, by the simultaneous use of such low molecular weight ethylene imine derivatives, products are frequently obtained which are similar to hard rubber, and have a low tear resistance. In some cases, the admixture of ethylene imine derivatives having a basis of polysiloxanes may be advisable.

The addition of monofunctional ethylene imine derivatives leads, in general, to less desirable mechanical properties, but a certain amount of such monofunctional derivatives is tolerable when the elastomers will not be exposed to higher mechanical stress. However, as a rule, the amount of bifunctional or higher functional ethylene imine derivatives should be at least 50%, preferably at least 80% by weight. In cases where a small amount of monofunctional material is present in the starting material was not entirely bifunctional, the elimination of the monofunctional ingredients is not always necessary.

The simultaneous use of protective agents against aging may be necessary with elastomers with polyether basis; such protectives being preferably antioxidants such as diphenylamine compounds. If such antioxidants contain groups capable of alkylation, or acidic groups, the above-mentioned statements should be observed. If such substances are, nevertheless used, it is preferable to apply them only to the finished shaped bodies or to make them pass into the same by diffusion.

The rubber-like products made according to the invention have a very wide range of



technical application, e.g. for elastic-shaped pieces of all types, as sealing means and coatings in electro-technical application for building purposes, in the production of automobiles, and for filling cracks and joints. They are also useful for making replicas, especially in dental medicine. As compared to the conventional materials, such as elastic silicone or "Thiokol" (Registered Trade Mark) based rubbers, they have the marked advantage of higher storability and absence of odour. As compared to silicone moulding materials, they have the added advantage that crosslinking will not become effective and increase the viscosity immediately after the addition of the crosslinking agent.

As compared with the widely used alginate moulding materials, the elastomers of the present invention have the advantage that replicas made therewith can be stored readily in air and can be cast repeatedly, whereas alginate replicas rapidly shrink in air and become useless. Replicas made with the elastomers of the present invention are therefore distinguished by their dimensional accuracy.

The materials may also be used advantageously for making soft linings of prostheses, particularly dental prostheses. Here the rapid crosslinking at room temperature is very useful. Due to this fact, a mixture of an ethylene imine compound with a highly active catalyst can be applied to the prosthesis and may be allowed to harden *in situ* within a few minutes, retaining an excellent accuracy of shape and thereby ensuring a first-class fit of the prosthesis. It will be understood that the only ethylene imine derivatives suitable for the lining of dental prostheses are those which do not have any readily hydrolysable bonds.

A further advantage of the elastomers of this invention is their good adherence and glueing property, particularly on glass, and their ability to be processed in combination with natural or synthetic organic or inorganic fabrics or fibres, even glass fibres. Their stability to cold is generally very good.

Foamed materials can be prepared from the modified polymers of this invention. Since no CO<sub>2</sub> is developed during the crosslinking reaction, contrary to the production of polyurethanes, it is necessary to use as blowing agents various organic solvents which evaporate during the foaming reaction, such as fluorohydrocarbons ("Freons") (Registered Trade Mark).

A further field of application provided by the unusual transparency of the elastomers of this invention is for optical purposes, e.g. for optical systems in general, for the production of lenses, or thin layers having satisfactory optical parameters, as well as for intermediate layers in safety glass.

When polymers with carboxyl groups are used as starting materials, the present invention has the added advantage that these are

generally easily accesible, and that the introduction of ethylene imine groups with formation of acid bonds is a reaction which usually proceeds very smoothly. This is an important factor since the introduction of ethylene imine groups by other routes frequently yields undesirable by-products which are difficult to remove, and which might disturb the crosslinking. It should also be noted that the acid amide bonds exhibit high stability to hydrolysis so that such elastomers, particularly those derived from polyethers, will be distinguished by such stability.

In this respect, they are superior to elastomers of a polyurethane basis which are known to contain biuret and allophanate groups whose stability to hydrolysis and to heat is not satisfactory.

It is surprising that the elastomers of this invention, particularly those which do not contain any aromatic radicals, are distinguished by high stability to light, a fact which was not to be expected in view of the amino groups contained therein.

The elastomers made according to the invention, particularly the last-mentioned ones, may also be obtained in the shape of highly elastic threads. Especially useful for practical applications are those substances which contain only ether groups and acid amide groups and, therefore, have no readily hydrolysable bonds.

A particular advantage of these elastomers is their rapid transition, even at comparatively low temperatures, from the plastic state, in which they are easily sprayed through nozzles, into the gel state, in which they can be wound as threads.

As mentioned before, the rapid transition and the capacity for spinning connection therewith, may be adjusted by the selection of the catalyst. It is also possible to add first a moderately active catalyst to the ethylene imine compound and to spin the mixture through nozzles into a bath containing a highly active catalyst dissolved therein.

If especially bright and high-grade products are desired, the ethylene imine derivatives should be purified by known means, such as filtration, if necessary in solution, over kieselguhr or aluminium oxide, or treatment with ion exchangers, washing solutions in organic solvents with water, aqueous alcohol, salt solutions, and the like, and, if necessary, repeated precipitation from, e.g., benzene or alcohols with cyclohexane or gasoline. A purifying effect can also be achieved by fractionation in known manner; this will also lead to products with a more uniform molecular weight.

The invention is illustrated in the following Examples.

#### EXAMPLE 1.

250 g. of polyester with terminal OH groups and a mean molecular weight of 7,200 made

70

75

80

85

90

95

100

105

110

115

120

125

130



from adipic acid with addition of 10 mol % sebacic acid and triethylene glycol, with addition of 10 mol % of hexanediol-1,6, are heated under nitrogen with 21 g. crotonic anhydride for one hour to 150° C., and for two hours to 180° C. Subsequently, the crotonic acid formed and excessive crotonic anhydride are removed by a vigorous current of N<sub>2</sub> at 2000° C.

50 g. of the resultant product are admixed with 8 g. ethylene imine at 55° C. and allowed to stand at room temperature for 7 days. The mass is then taken up in benzene, washed several times with water and, after drying of the organic phase, the solvent and excessive ethylene imine are removed by application of high vacuum at 50° C. There are obtained 38.5 g. of a light yellow oil having an amine equivalent of 3,900 and a viscosity of 2,900 poises/25° C.

1 g. of the ethylene imine compound is mixed with 0.06 g. benzene sulphonic acid methylester; after several minutes the viscosity increases, and after about 20 minutes a transparent body of rubber like elasticity has been formed whose elastic properties remain unchanged over a considerable period.

#### EXAMPLE 2.

0.5 g. of the ethylene imine compound made according to Example 1 is mixed with 0.03 of a mixture containing 4 parts *p*-toluene sulphonic acid methylester and 1 part *p*-chlorobenzene sulphonic acid methylester. Gelling sets in after about 1.5. minutes and after about 6 minutes, the rubber-elastic is reached

#### EXAMPLE 3.

1. g. of ethylene imine compound made according to Example 1 is mixed with 0.06 g. of a 20% solution of 2.5 dichlorobenzene-sulphonic acid methylester in diamyl phthalate. After about 4 minutes, there is obtained at room temperature a transparent mass having permanent rubber-elastic properties.

#### EXAMPLE 4.

100 g. of the polyester mentioned in Example 1 are heated with 7.0 g. acrylic anhydride and 1 g. copper powder in a CO<sub>2</sub> atmosphere for one hour to 140° C. Subsequently, a strong current of CO<sub>2</sub> is blown through the reaction mixture at 160° C. for 3 hours. After cooling the mass is taken up in benzene, the undissolved portion is separated by centrifugation, and the benzene solution concentrated *in vacuo*.

50 g. of the resultant product are mixed with 3 ml triethylamine and 2.5 g. ethylene imine. After standing for 6 days at room temperature the substance is taken up in benzene, and solvent, triethylamine and excessive ethylene imine are sucked off in a high vacuum. There are obtained 49.5 g. of a slightly coloured green-brown oil having a base equivalent of 3,200.

Dissolved copper can be removed by shak-

ing the benzene solution with an aqueous solution of ethylene diamine-tetra acetic acid disodium salt.

1.0 g. of the resultant ethylene imine compound is mixed with 50 mg. benzene sulphonic acid methyl ester. After about 3 minutes, the mass is noticeably more viscous and becomes, after about 12 minutes, rubber-elastic.

#### EXAMPLE 5.

2.0 of the ethylene imine compound formed in Example 4 are mixed with 0.05 g. of a mixture consisting of equal parts of 2,5-dichloro-benzene sulphonic acid methyl ester and diethylene glycol dimethyl-ether. Cross-linking starts after about 1 minute, and is substantially complete after about 5 minutes.

#### EXAMPLE 6.

720 g. of a polyester prepared from adipic acid pimelic acid and triethylene glycol in a water ratio 1:0.15:1.35, which contains terminal OH-groups and has a mean molecular weight of 1600, are heated with 230 g. crotonic anhydride for one hour to 150° C and for one hour to 200° C. Subsequently excess crotonic anhydride is blown off at 200° C. The resultant polyester having crotonic acid terminal groups has a viscosity of about 80 poises at 25° C.

To 100 g. of this product, 54 g. ethylene imine are added dropwise at 50° C; after 5 days standing at room temperature the mass is dissolved in benzene, washed repeatedly with water and the organic phase evaporated to dryness *in vacuo*. 76 g. of oil are obtained having an ethylene imine equivalent of 950.

1.0 g. of the resulting ethylene imine compound is mixed with 0.08 g. *p*-toluene sulphonic acid methyl ester. After about 30 minutes a transparent rubber-elastic mass has formed.

#### EXAMPLE 7.

100 g. of a polyethylene glycol of mean molecular weight 4000 are heated with 12 g. of crotonic anhydride for 1 hour at 150° C and for 1 hour at 180° C. Volatile ingredients are subsequently completely blown out at 200° C by means of CO<sub>2</sub>. A substance is obtained which is of war-like consistency at room temperature.

50 g. of this product are melted at 50° C and after addition of 10 ml benzene are admixed with 10 g. ethylene imine and are heated to 35° C for 4 days. Solvent and excess ethylene imine are drawn off *in vacuo*. There are obtained 47.5 g. of a wax-like substance.

2.0 g. of this substance are mixed at 70° C with 0.12 g. *p*-methoxybenzene sulphonic acid methyl ester. Cross-linking starts immediately and leads in several minutes to a product of hard rubber-like properties.

#### EXAMPLE 8.

113 g. of a polyester with terminal OH groups and a mean molecular weight of 2900,

prepared from adipic and sebacic acids in a molar ratio of 1:1 and triethylene glycol with the addition of 10% tetraethylene glycol, are reacted with 19 g. crotonic anhydride, as described in Example 1

105 g. of the product are allowed to stand with 31 g. ethylene imine and 25 g. triethylamine for 10 days. The mass is then dissolved in 100 ml benzene, filtered, and dried in vacuo at 60° C. The product has a viscosity of about 100 poises/25° C and an amine equivalent of 1670. After the addition of 6% by weight of benzene sulphonic acid methyl ester, rubber elasticity results in about 15 minutes.

#### EXAMPLE 9.

50 g. of a branched polyester prepared from adipic and sebacic acids, trimethylolethane and triethylene glycol, in a molar ratio 9:1:0.67:11, and having a viscosity of 140 poises at 25° C, are heated with 15.6 g. crotonic anhydride for 1 hour at 150° C and one hour at 200° C. Subsequently the volatile portions are blown out with CO<sub>2</sub> at 210° C.

50 g. of the product are stirred with 25 g. triethylamine and 27 g. ethylene imine for 5 days. Subsequently the mass is dissolved in benzene and brought to dryness at 60° C using a high vacuum in the later stages. There are obtained 51.5 g. of an ethylene imine compound having an equivalent weight of 1080.

1.0 g. of the ethylene imine compound is mixed with 0.06 g. benzene sulfonic acid methyl ester. A solid rubber is obtained after 15 minutes.

If 10 g. of the ethylene imine compound is mixed with 0.12 g. of a 20% solution of 2,5-dichlorobenzene-sulphonic acid methyl ester in diamylphthalate, the rubber-elastic state is reached after about 3 minutes. It remains unchanged after considerable storage time.

#### EXAMPLE 10.

(a) 0.5 g. of the ethylene imine compound described in Example 1 is mixed with 30 mg benzene sulphonic acid ethyl ester and kept at 50° C. After about half an hour, cross linking has noticeably set in and becomes complete after several hours.

(b) When the same ethylene imine compound is mixed with 6% methane sulphonic acid methyl ester, the rubber-elastic state is reached after about 40 minutes.

(c) 1.0 g. of the ethylene imine compound mentioned in Example 1 is mixed with 0.1 g. of a 20% solution of dimethyl sulphate in diamylphthalate. Gelling sets in after a very short time and is practically complete after about 3 minutes. A mass of good, permanent elasticity is obtained.

(d) When the same ethylene imine compound is mixed with 6% diethyl sulphate, gelling sets in after about 15 minutes and is complete after 1 to 2 hours.

(e) A mixture of 2.0 g. of the ethylene imine compound described in Example 1 with 0.12 g. phosphoric acid soon starts to gel and has reached a rubber-like state after about 4 hours.

#### EXAMPLE 11.

The polyester mentioned in Example 1 is reacted with crotonic anhydride as described therein. To 460 g. of the product a mixture of 80 ml triethylamine and 90 ml benzene is added while stirring at 55° C. Subsequently 69 g. ethylene imine are added drop by drop. After standing for 6 days at room temperature the volatile portions are removed at 50° C. using a high vacuum in the later stages. There are obtained 465 g. ethylene imine compound having an amine equivalent of 3650 and a viscosity of about 1200 poises/25° C.

To produce a moulding paste for replicas, 50 g. of the product are kneaded with 12.5 g. kieselgur and 1.2 g. zinc white.

A cross-linking paste is made by kneading 80 g. dioctyl phthalate, 20 g. 2,5-dichlorobenzene sulphonic acid methyl ester, 16 g. "Aerosil" (Registered Trade Mark) and 1 g. cadmopur red.

For making mouldings, particularly in dental medicine, the two pastes are mixed in a ratio of about 5:1, until an even red colour is reached. Setting starts at about 2½ minutes and is complete after about 4 more minutes at 36° C.

#### EXAMPLE 12.

82 g. of a polyester made from adipic acid, sebacic acid, trimethylol propane and triethylene glycol, in a molar ratio of 9:1:0.33:10.5, are heated with 13 g. crotonic anhydride for one hour at 150° C. and for four hours of 180° C. The mass is dissolved in benzene, shaken several times with sodium hydroxide, washed with water and dried in vacuo. Yield: 67 g.

35 g. of the product are mixed with 10 g. triethylamine and are further mixed at 50° C. with 10.5 g. ethylene imine. After 6 days the mass is dissolved in benzene and dried at 50° C in vacuo.

1g. of the resultant ethylene imine compound, which has an amine equivalent of 1535, is mixed with 0.06 g. of benzene sulphonic acid methyl ester. After about 15 minutes, a rubber-elastic mass is obtained having an elasticity which does not change after a long period.

#### EXAMPLE 13.

570 g. of a mixed polymer of tetrahydrofuran and ethylene oxide in a molar ratio of 1:1, which has a mean molecular weight of 3600, are heated in a CO<sub>2</sub> atmosphere with 46 g. crotonic anhydride for one hour to 150° C. and for one hour to 180° C. The volatile portions are removed subsequently by blowing at 200° C.

355 g. of the so obtained substance are

mixed with 92 ml. triethylamine and 76 g. ethylene imine at 50° C. After allowing to stand for 7 days at room temperature the mass is taken up in chloroform, washed thoroughly, dried over potassium carbonate, filtrated, and dried *in vacuo*. Yield: 281 g. ethylene imine compound having a base equivalent of 1920.

For making a moulding paste, 100 g. of the ethylene imine compound, 5 g. dibutylphthalate, and 50 g. kieselgur are kneaded together. When this paste is mixed with the cross-linking paste described in Example 11 in a ratio 4:1, the rubber-elastic state is reached after a few minutes.

For mucostatic replica-making in dental medicine, where a slow setting is desired, the two pastes are mixed in a ratio 7:1.

#### EXAMPLE 14.

250 g. of a polyester with an OH-equivalent of 1380 prepared from adipic acid with an addition of 10 molar % sebacic acid, and butane diol-1,3 with addition of 8 mol. % hexane diol-1,6, are heated in a CO<sub>2</sub> atmosphere with 85 g. crotonic anhydride for 2 hours at 180° C and for 4 hours at 200° C. After blowing off the volatile portions, 60 g. triethyleamine and 65 g. ethylene imine are admixed at 45° C and are allowed to stand for 7 days at room temperature. The mass is taken up in chloroform, thoroughly washed with water, desiccated, filtered and brought to dryness. Yield: 205 g. ethylene imine compound having a base equivalent of 1520.

1.0 g. of the ethylene imine compound is mixed with 0.08 g. benzene sulphonic acid methyl ester and after 30 minutes a rubber-elastic mass has been formed.

#### EXAMPLE 15.

N - (N' - isopropyl - aminopropyl) - ethyleneimino-acetamide is made by allowing to stand for 3 days at room temperature a mixture of 0.45 mol. ethyleneimino-acetic ester and 1.36 mol.  $\gamma$ -isopropylamino propylamine. Distilling *in vacuo* gives 59 g N-N'-isopropyl-aminopropyl)-ethyleneimino-acetamide having a boiling point of 110 to 113° C at 0.1 mm pressure.

0.034 g. zinc-propionyl-acetophenoate are dissolved in 34.2 g. of copolymer of ethylene oxide and tetrahydrofuran in molar ratio 1:1 having a mean molecular weight of 5700 and 2.61 g. toluylene-2, 4-diisocyanate are added at 18° C. after 15 minutes, 3.58 g. N-N'-isopropyl - aminopropyl) - ethyleneimino-acetamide are added drop by drop at 20° C and are further stirred for 15 minutes.

When 2.0 g. of the so obtained ethylene imine compound are mixed with 0.12 g. benzene sulphonic acid methyl ester, gelling sets in after a few minutes, and after about 20 minutes a clear, transparent product of high permanent elasticity has formed.

#### EXAMPLE 16.

0.014 mg. zinc-propionyl-acetophenoate are dissolved at 40° C. in 14 g. of the poly-

ester mentioned in Example 1, and 0.87 toluylene-2, 4-diisocyanate are added at 20° C. The mixture is stirred at room temperature for one hour, and then 1.19 g. N-N'-isopropyl-aminopropyl)-ethyleneimino-acetamide is added. The reaction is terminated after a few minutes.

A mixture of 1.0 g. of the resultant ethylene imine compound and 0.07 g. benzene sulphonic acid methyl ester quickly gels and reaches the rubber-elastic state after about 20 minutes.

#### EXAMPLE 17.

1.52 of toluene-2,4-diisocyanate is added at room temperature to a solution of 0.020 g. zinc propionyl acetophenonate in 20.0 g. of a copolymer of ethylene oxide and tetrahydrofuran in molar ratio 1:1, and having a mean molecular weight of 5,700 and after 15 minutes 1.04 g  $\gamma$ -ethylene imino propylamine is also added with stirring. Stirring is continued for another 15 minutes at room temperature, and after addition of 6% of benzene sulphonic acid methyl ester the resulting ethylene imine compound becomes rubber-elastic after about 15 minutes.

#### EXAMPLE 18.

A polyester made from adipic acid, sebacic acid, hexane diol-1,6 and triethylene glycol in molar ratio 18:2:15:6, is treated with crotonic anhydride as described in Example 1.

200 g. of this product are mixed at 50° C with 42 ml. triethylamine and 35 g. ethylene imine and allowed to stand for 6 days at room temperature. Then the mass is taken up in chloroform, thoroughly washed and dried over potassium carbonate. After filtration and removal of the solvent *in vacuo*, 185 g. of a wax-like substance are obtained having a base equivalent of 2600.

When 5 g. of this substance are melted at 40° C and mixed with 0.06 g. of a 20% solution, 2,5-dichlorobenzene sulphonic acid methyl ester in dioctyl phthalate, a solid rubber forms after a few minutes having good tear resistance and permanent elasticity.

#### EXAMPLE 19.

By mixing 2 parts of the ethylene imine compound described in Example 18, with 1 part dioctylphthalate, a slightly turbid mass is obtained. When 7.5 g. of this mass is mixed with 0.6 g. of a 20% solution of 2,5-dichlorobenzene sulphonic acid-methyl ester in diamyl phthalate, cross-linking is noticeable after a few minutes by the increase in viscosity. After about 15 minutes, a highly elastic rubber has formed.

#### EXAMPLE 20.

A copolymer of tetrahydrofuran and ethylene oxide in the molar ratio of 2:1 and having a mean molecular weight of 6600, is converted as before with crotonic anhydride. To 52 g. of the product a mixture of 3 g. triethyl-

amine and 3.35 g. ethylene imine is added at 50° C and stirred. After 11 days of standing at room temperature, a large amount of the amines is removed *in vacuo* at 50° C. and the remaining mass dissolved in chloroform. After washing, drying and elimination of the solvent, with application of high vacuum in the last stage, 45.5 g. of an ethylene imine compound are obtained having a base equivalent of 3270.

1.0 g. of this substance is mixed with 0.1 g. of equal parts of 2,5-dichloro-benzene sulphonic acid methyl ester and diethylene glycol-dimethylether. After about 20 minutes, a rubber-elastic substance has formed.

#### EXAMPLE 21.

0.03 g. dibutyltin dilaurate were added at 0° C. to a mixture consisting of 28.5 g. of a copolymer of tetrahydrofuran and ethylene oxide in the molar ratio 3:1 with a mean molar weight of 5700, 2 ml. ethylene glycol dimethyl ether and 1.96 g. toluylene-2,4-diisocyanate. After allowing to stand at 0° C. for one hour, 2.69 g. N-(N'-isopropylene-amino propyl)-ethyleneimino-acetamide were added slowly drop by drop. The mixture is then allowed to warm up to room temperature, dissolved in 100 ml. chloroform, repeatedly washed with water, dried by potassium carbonate and finally dried *in vacuo*. Yield: 20.05 g. ethylene imine compound with a base equivalent of 2970.

For making a lens, 1.5 g. of the substance are mixed with 0.095 g. benzene sulphonic acid methyl ester and brought into a suitable mould. After 30 minutes, the article is removed from a mould and a lens is obtained having a high scratch resistance and whose focal length can be reversibly changed by deformation.

#### EXAMPLE 22.

A polyester made from adipic acid, maleic anhydride, hexanediol-1,6, butanediol-1,3 and decanediol-1,10 in molar ratio 17:3:16:3:2, is provided with crotonic acid terminal groups as described above.

A mixture of 30 g. triethylamine and 43 g. ethylene imine is added at 45° C with stirring to 154 g. of this substance and allowed to stand at room temperature for 5 days. Subsequently, the mass is taken up in chloroform and processed as usual. Yield: 134 g. of an ethylene imine compound having a base equivalent of 1660.

The product, which is wax-like at room temperature, is melted at 35° C and 1.0 g. is mixed with 0.14 g. of a mixture of equal parts of *p*-toluene-sulphonic acid methyl ester and dioctylphthalate. After several minutes, a stiff rubber-elastic substance has formed.

#### EXAMPLE 23.

60.0 g. of a copolymer of tetrahydrofuran and ethylene oxide, in molar ratio 1:1, with a mean molar weight of 2000, are mixed with a solution of 4.2 g. naphthalene-1, 5-

diisocyanate in 60 ml. ethylene glycol-dimethyl ether at 30° C; subsequently, 0.25 ml. dibutyl tin dilaurate is added and the mixture allowed to stand for 20 hours at 25° C. Subsequently, 3.94 g. toluylene-2, 4-diisocyanate are added dropwise at 0° C. with stirring, and stirring is continued at that temperature for 4 hours, 5.2 g. N-(N'-isopropylaminopropyl) - ethyleneimino - acetamide are then added and the mass is allowed to come to room temperature, taken up in chloroform, and after the conventional purification, yields 60.5 g. of an ethylene imine compound having an equivalent weight of 3830. A mixture of 1.0 g. of this substance and 0.05 g. of a solution of 1 part 2,5-dichloro-benzene sulphonic acid methyl ester in 2 parts diamylphthalate begins rapidly to gel and is transformed after a few minutes into a solid rubber of permanent elasticity.

#### EXAMPLE 24.

A copolymer of tetrahydrofuran and ethylene oxide in molar ratio 2:1 with an OH equivalent 1760, is provided with acrylic terminal groups in the manner described in Example 4. To 50 g. of this substance, a mixture of 3.0 g. triethylamine and 3.45 g. ethylene imine is added at 50° C while stirring. After 10 days standing at room temperature, processing is effected in the usual manner. Dissolved copper is removed by shaking with an aqueous solution of the disodium salt of ethylene diamine-tetra acetic acid. Yield: 36.7 g. ethylene imine compound having a base equivalent of 1945.

2.0 g. of this substance yield a stiff rubber about 10 minutes after mixing with 0.24 g. of a mixture of 40 parts *p*-chloro-benzene sulphonic acid methyl ester and 60 parts diamylphthalate.

#### EXAMPLE 25.

1.0 g. of the ethylene imine compound described in Example 1 is mixed with 0.10 g. of the boron-trifluoride-N,N-dimethyl acetamide complex compound. Cross linking occurs very soon. The mass is heated to 50° C. for about 5 minutes and passes into the rubber-elastic state.

#### EXAMPLE 26.

0.5 g. dibutyl tin dilaurate is dissolved in 121.5 g. propylpropylene glycol of mean molar weight 2000, and 10.8 g. diphenylmethane-4, 4'-diisocyanate are added dropwise at 0° C. with stirring. Subsequently, the mixture is allowed to warm to room temperature and to stand at this temperature for 20 hours.

A solution of 3.68 g. toluylene-2, 4-diisocyanate and 0.08 g. dibutyl tin dilaurate in 17 ml. ethyleneglycol-dimethyl ether is added dropwise at 0° C. with stirring to 60 g. of this mixture and stirring continued for 4 hours at the same temperature. 4.8 g. N-(N'-isopro-

pyl-aminopropyl)-ethyleneimino-acetamide are added at 0° C, and the mass is allowed to warm to room temperature, taken up in methylene chloride, washed thoroughly with water, dried over potassium carbonate, and finally the solvent driven off in a high vacuum. Yield: 41.5 g. ethylene imine compound having a base equivalent of 3850.

- 5 0.8 g. of this ethylene imine compound  
10 are stirred with 0.015 g. of a mixture of 10 parts 2,5-dichloro-benzene sulphonic acid methyl ester and 3 parts diethylene-glycol-dimethylether. After a few minutes, the mixture has rubber-like consistency.

#### EXAMPLE 27.

- 15 N - (N' - isopropyl - aminopropyl) -  $\alpha$ -ethylene imine-butyramide is prepared by heating a mixture of 0.2 mol  $\alpha$ -ethylene imine-butyric methylester, 0.6 mol.  $\gamma$ -isopropyl-amino-propylamine and 15 ml. methanol under reflux for 2 days at 70° C. By rectifying C. at 0.1 mm.

- 20 in *vacuo*. 17 g. N-(N'-isopropyl-amino-propyl)- $\alpha$ -ethylene imine-butyramide are obtained having a boiling point of 115 to 118°

- 25 45.0 g. of a copolymer of tetrahydrofuran and ethylene oxide in a molar ration 3:1 and a mean molecular weight of 4,500 are mixed with 13 ml. anhydrous ether. Subsequently,  
30 3.93 g. toluylene-2, 4-diisocyanate and 0.11 g. dibutyl tin dilaurate are added at 0° C. and allowed to stand for 4 hours at this same temperature. 12 ml. ether are stirred into the reaction mixture, and the mixture divided into  
35 portions.

- Into 34.0 g. of this mixture there are mixed 3.12 g. of N-(N'-isopropyl-aminopropyl)- $\alpha$ -ethylene imine-butyramide at -2° C. with stirring. The mixture is allowed to reach  
40 room temperature, taken up in 250 ml. ether and after repeated washing, drying over potassium carbonate, and removal of the solvent, yields 15.6 g. ethylene imine compound having a base equivalent of 2620.

- 45 2.0 g. of this product are mixed with 0.4 g. of a mixture of *p*-chloro-benzene sulphonic acid methyl ester and benzene sulphonic acid methyl ester in the ratio of 1:1. Cross-linking sets in after about 3 minutes: after about 10  
50 minutes, a rubber-elastic body is formed.

#### EXAMPLE 28.

- 26.4 g. of the reaction mixture mentioned in Example 27, second paragraph, are mixed with 0.85 g.  $\beta$ -ethylene imino ethanol at 0° C. and allowed to stand at room temperature for  
55 24 hours. 200 ml. ether are then added, the solution is repeatedly washed with water and the solvent is removed by high vacuum. Yield: 15.8 g. ethylene imine compound with amine equivalent 3130.

- 50 3 g. of this substance are mixed with 0.06 g. of a mixture containing equal parts *p*-chloro-benzene sulphonic acid methyl ester

and benzene sulphonic acid methyl ester. About 15 minutes a viscous rubber-like mass has formed having high permanent elasticity. 65

#### EXAMPLE 29.

A co-polymer of tetrahydrofuran, ethylene oxide, and 4-bromobutene oxide-1,2 in the molar ratio of 100:30: 4 is prepared according to the process of W. J. Murbach and A. Adicoff, Ind. Eng. Chem. 52 772 (1960). The product has a bromine equivalent of 1910. For exchanging the bromine atoms by amino groups, 64.4 g. of the copolymer dissolved in 98 g. dimethylformamide, and heated with 8.4 phthalimide potassium for 34 hours to 80° C. The mixture is then stirred into 500 ml. water and the precipitate is reprecipitated twice from ethylene glycol monomethyl ether with water. The precipitate is again dissolved in a large quantity of ethylene glycol monomethyl ether and the adhering water is removed by distilling off the ethylene glycol monomethyl ether *in vacuo*. 70 75 80 85

The resulting solution in ethylene glycol monomethyl ether (650 ml) is heated with 2.73 ml. of an 80% aqueous solution of hydrazine hydrate for 2½ hours at 80° C. After distilling off 200 ml. methylglycol *in vacuo*, 270 ml. 2 N. acetic acid are added and the mixture is refluxed for an hour. After sucking off the phthalic hydrazide which has formed, 630 ml. methanol and 400 ml. water are added to the filtrate which is allowed to pass through a column charged with a strongly basic ion exchanger (OH form). The solution is then concentrated *in vacuo* and shaken with methylene chloride after addition of 30 ml. of 30% sodium hydroxide. After removal of the solvent, 35 g. of polyamine are obtained having an amine equivalent of 2220. 90 95 100

8.88 g. of this substance are heated with 4.6 g. ethylene imino acetic acid methylester, 5.0 g. glycol and 10 ml. methanol for 34 hours to 50° C. The reaction mixture is taken up in 130 ml. methanol and precipitated with 500 ml. water and after centrifuging is taken up in ether. After drying an evaporation of the solvent, 6.8 g. of poly(ethylene imine) compound are obtained. 105 110

2.0 g. of this product are mixed with 0.13 g. of a mixture consisting of 10 parts 2,5-dichloro-benzene sulphonic acid methyl ester and 3 parts diethyleneglycol-dimethylether. After a short while, cross-linking sets in and leads, after about 20 minutes, to a rubber-elastic product. 115

#### EXAMPLE 30.

150 g. of a polyether (prepared from tetrahydrofuran, ethylene oxide,  $\omega$ -epoxy-decanoic methyl ester and BF<sub>3</sub> as initiator, in molar ratio 120:32:8:1) having a mean molecular weight of 8,700 and an ester equivalent of 1,050 are allowed to stand for 4 days at room temperature with 50 g. methanol, 90 g.  $\gamma$ -ethylene imino propylamine and 10 ml. 120 125

potassium glycolate solution (prepared by dissolving 1 g. potassium in 100 ml. ethylene glycol). 300 ml. methanol are added and the mixture purified by stirring with an acid ion exchanger, precipitating with water and reprecipitating from ethylene glycol-dimethylether with water. The resulting oil is taken up in benzene, dried over potassium carbonate and the solvent is finally removed by a high vacuum. Yield: 82.5 g. ethylene imine compound in form of a colourless oil having a base equivalent of 1910.

2.5 g. of this compound are mixed with 0.3 g. of a 20% solution of 2,4-dichlorobenzene sulphonic acid methyl ester in dioctylphthalate. After about 20 minutes, a transparent rubber-like mass has formed having a high permanent elasticity.

#### EXAMPLE 31.

When the mixture of polyether,  $\gamma$ -ethylene imino propylamine, etc., described in Example 30, is allowed to stand for 8 days at room temperature, there is obtained after appropriate processing an ethylene imine compound having a base equivalent of 1200.

A mixture of 2 g. of this product with 0.25 g. of a 20% solution of 2,4-dichlorobenzene sulphonic acid methyl ester in dioctylphthalate rapidly starts to gel and after about 10 minutes is transformed into a solid rubber.

#### EXAMPLE 32.

300 g. of a polyether (prepared from tetrahydrofuran, ethylene oxide,  $\omega$ -epoxy-undecanoic methylester and  $\text{BF}_3$  as initiator, in molar ratio 100:50:8:1), having a mean molecular weight of 9400 and an ester equivalent of 980, are heated with 400 g. methanol, 180 g.  $\gamma$ -ethylene imino propylamine and 40 g. glycol for 10 days at 50° C. Subsequently, the mass is taken up in 600 ml. methanol and worked up as described in Example 30. Yield: 241 g. of a viscous oil having a base equivalent of 1080.

4 g. of the resulting ethylene imine compound are mixed with 0.5 g. of a 20% solution of 2,4-dichlorobenzene sulphonic acid methyl ester in dioctylphthalate. After half an hour, a rubber-elastic mass has been formed.

#### EXAMPLE 33.

60 g. of a polyether made from tetrahydrofuran and ethylene oxide in a molar ratio 2:1, having a mean molecular weight of 9750, and having been provided with methyl ester terminal groups by reaction of the terminal OH groups with isocyanate acetic ethylester in a manner known per se, are dissolved in 30 ml. methanol and heated with 3.6 g. ethylene imino propylamine for 42 hours at 50° C. Subsequently the mixture is taken up in 200 ml. methanol, precipitated with a large amount

of water, the separated oil dissolved in benzene, and the solvent is evaporated after drying *in vacuo*. The residue weights 52.5 g. and has a base equivalent of 5150.

When 2 g. of this ethylene imine compound are heated to 50° C. with 0.3 g. of a 20% solution of 2,4-dichlorobenzene sulphonic acid methyl ester in diamylphthalate, a rubber elastic body is formed after 10 minutes.

#### EXAMPLE 34.

20 g. of the polyether described in Example 33 are allowed to stand for four days at room temperature with 10 ml. methanol and 1.9 g.  $\omega$ -ethylene imino heptylamine (made from  $\omega$ -bromoenanthis nitrile by reaction with ethylene imine and subsequent hydrogenation with lithium-alanate). After addition of 10 ml. methanol, a large amount of water is used for precipitation and the oil thus obtained is taken up in ether. After drying over potassium carbonate, precipitation is effected with low-boiling gasoline and the isolated oil freed from solvent *in vacuo*. Yield: 17.7 g. ethylene imine compound with a base equivalent of 5850.

A mixture of this substance with 2% by weight of benzene sulphonic acid methyl ester assumes a rubber-like consistency after about 20 minutes standing at 80° C.

#### EXAMPLE 35.

3 g. of the ethylene imine compound described in Example 34 are mixed with 0.06 g. *m*-chlorobenzene sulphonic methyl ester. The mixture is converted into a solid rubber after about 30 minutes at 50° C.

#### EXAMPLE 36.

67.3 g. of a polyester prepared from adipic acid, azelaic acid and 1,6-hexane diol in molar ratio 7:7:13, having a substantial number of carboxyl terminal groups and a mean molecular weight of 3370, are dissolved in 34 ml. pyridine together with 21.9 g. di-*p*-nitrophenylcarbonate and heated for 2½ hours at 60° C. The yellow syrup which forms is stirred into a mixture of 200 ml. ethyleneglycol dimethylether, 200 ml. methanol and 200 ml. of a strongly basic ion exchanger. Subsequently 10.0 g.  $\gamma$ -ethylene imino-propylamine are added drop by drop and stirring is continued for 30 minutes. After filtration, pyridine and by-products are removed by passing the solution through columns of acid and basic ion exchangers, respectively, and drying is performed *in vacuo*.

2.0 g. of the resultant ethylene imine compound are mixed with 0.04 g. benzene sulphonic acid methyl ester at 50° C. When a mixture is further heated to 50° C, gelling sets in after about 3 minutes and gradually yields a rubber-elastic product. If the mixture is heated to 80° C. a dry rubber-elastic body is obtained after about 3 minutes.



## EXAMPLE 37.

82.4 g. of a polyester prepared from equimolar amounts of pimelic and glutaric acids, and 1,3-propanediol and 1,6-hexane diol, respectively, and having primarily terminal carboxylic groups and a mean molecular weight of 4120, are heated with 40 ml. pyridine and 21.9 g. di-nitrophenylcarbonate for 3 hours to 65° C. The light-brown syrup formed is reacted and worked up as described in Example 36 with 10.0 g.  $\gamma$ -ethylene imino propylamine. Yield: 67.4 g. ethylene imine compound in the form of a slightly brown coloured oil.

3.0 g. of this product are mixed with 0.06 g. *m*-chloro-benzene sulphonic acid methyl ester, and cross-linking is substantially completed after 5 minutes at 80° C. with formation of a rubber-elastic body.

## EXAMPLE 38.

13.4 g. of the polyester formed according to Example 36 are dissolved in 20 ml. ethyleneglycol dimethylether, mixed with a solution of 0.8 g. N,N'-carbonyl-diimidazol in 30 ml. ethyleneglycol dimethylether, and the mixture allowed to stand at room temperature for 2½ hours. Subsequently a solution of 1.52 g.  $\gamma$ -ethylene imino propylamine in 5 ml. ethyleneglycol dimethylether is added. After 10 minutes, the solvent is removed *in vacuo* and the residue taken up in 150 ml. benzene. The imidazol formed is eliminated by repeated shaking with water. Finally, the benzene solution is dried over potassium carbonate and freed from the solvent *in vacuo*. The ethylene imine compound formed is almost colourless and wax-like at room temperature.

4 g. of this substance are melted at 50° C and 0.12 g. *m*-chloro-benzene sulphonic acid methyl ester added. Gelling then sets in after 5 minutes, and after about one hour a rubber-elastic mass has formed.

## EXAMPLE 39.

67.3 g. of the polyester mentioned in Example 36 are dissolved in 100 ml. benzene. 6.1 ml. of triethylamine are added followed by 18.9 g. bis-2,4-dinitrophenyl carbonate, and the mass is then allowed to stand for 4 hours. Thereafter 400 ml. benzene and 200 ml. of a basic ion exchanger are added, and 6.8 of 3-ethylene imino-propylamine are added drop by drop with continuous stirring for 30 minutes. After passing a mixed-bed column and concentration by evaporation there is obtained 54.6 g. of a light yellow viscous oil which solidified to a wax-like mass at room temperature.

3 g. of this product are mixed with 0.09 g. of *p*-toluene sulphonic methylester at 45° C. Cross-linking with formation of a transparent rubber-elastic body, starts after about 3 minutes, and is completed after 2 hours heating to 60° C.

## EXAMPLE 40

364 g. polyetherdiol-bis-chloroformate of a mean molecular weight 9,100 (prepared from a copolymer of tetrahydrofuran and ethylene oxide by known reaction with phosgene) are added with stirring at -5° C. to 0° C. to a solution of 8.8 g. 3-ethylene imino-propylamine and 8.9 g. triethylamine in a mixture of 500 ml. benzene and 100 ml. ethyleneglycol dimethylether and stirring continued for 2 hours at 0° C. After addition of 300 ml. benzene, passage through a mixed-bed column and concentration by heating, the last stage being *in vacuo*, a colourless oil is obtained having a base equivalent of 8250.

5 g. of this ethylene imine compound are mixed with 0.15 g. *m*-chloro-benzene sulphonic acid methyl ester and heated to 60° C. for 30 minutes to yield in a rubber-elastic mass.

## EXAMPLE 41.

2.02 g. triethylamine and 1.33 g *p*-nitrophenol dissolved in 25 ml. of ethylene glycol dimethylether are added drop wise to a solution of 37.6 g. polyetherdiol-bis-chloroformate with a molecular weight of 9400 in 120 mol. ether. The precipitate formed is removed by centrifugation, and after addition of 50 ml. basic ion exchanger there are added with stirring to this solution 1.54 g. of 5-ethylene imino pentylamine dissolved in 10 ml. ether. Further processing is carried out as in Example 40 yielding 32.4 g. of a slightly yellow oil having a base equivalent of 5720.

A mixture of the resulting substance with 3% *m*-chlorobenzene sulphonic acid methyl ester yields a rubber-elastic mass after about 10 minutes heating to 60° C.

## EXAMPLE 42.

4 g. of the ethylene imine compound described in Example 13 are mixed with 0.2 g. tetrapropylene-benzene sulphonic acid. After a short while, gelling sets in, which leads in about 5 minutes to a rubber-elastic body.

## WHAT WE CLAIM IS:—

1. Modified polymers which are predominantly linear polyesters, polyethers or polythioethers containing on average more than one ethylene imine group per molecule and having a mean molecular weight of at least 1,000 and an ethylene imine equivalent of at least 500.

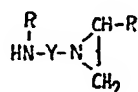
2. Modified polymers according to claim 1, which contain on average up to 5 ethylene imine groups per molecule, and have a mean molecular weight of 3,000 to 25,000 and a viscosity not greater than 30,000 poises at 70° C.

3. Modified polymers according to claim 1 or 2, which have an ethylene imine equivalent of 1,000 to 8,000 and a viscosity of 1 to 30,000 poises at 25° C.

4. Modified polymers according to claim 125

1, 2 or 3, which contain on average 1.8 to 2.5 ethylene imine groups per molecule and have a mean molecular weight of 6,000 to 15,000 and a viscosity between 10 and 10,000 poises at 25° C.

- 5 A process for the preparation of the modified polymers claimed in any one of claims 1 to 4, wherein a polyester, polyether or polythioether containing carboxyl groups  
10 or amide-forming derivatives thereof is reacted with an ethylene imine derivative of the formula:



- 15 wherein R represents a hydrogen atom or an alkyl group and Y represents a bivalent organic radical.

6. A process according to claim 5, wherein the polyester, polyether or polythioether used as starting material contains carbomethoxy, carboaryloxy, N-acyl or chloroformate groups.

- 20 7. A process according to claim 6, which comprises reacting a polyester, polyether or polythioether containing hydroxyl groups with phosgene, and reacting the resultant chloroformate derivative with the ethylene imine derivative.

- 25 8. A process for the preparation of the modified polymers claimed in any one of claims 1 to 4, wherein a polyester, polyether or polythioether containing hydroxyl groups is reacted with a difunctional intermediate compound in which one function will react with a hydroxyl group and the other with a hydroxyl group, and/or an amino group  
30 and the resultant derivative is reacted with ethylene imine or an ethylene imine substituted amine or alcohol.

- 35 9. A process according to claim 8, wherein the intermediate compound is an unsaturated carboxylic acid.

- 40 10. A process according to claim 9, wherein the unsaturated carboxylic acid is crotonic or acrylic acid.

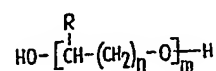
- 45 11. A process according to claim 8, wherein the intermediate compound is a halogen-substituted carboxylic acid.

12. A process according to claim 11, wherein the halogen-substituted carboxylic acid is monochloroacetic acid or  $\alpha$ -bromobutyric acid.

- 50 13. A process according to claim 8, wherein the intermediate compound is a diisocyanate.

14. A process according to claim 13, wherein the diisocyanate is 2,4-tolylene-diisocyanate, 4,4'-diphenylmethane-diisocyanate, naphthalene-1,5-diisocyanate or hexane-1,6-diisocyanate.

15. A process according to any one of claims 7 to 14, wherein a polyether of the  
60 formula:



wherein  $n=1-3$ ,  $m=25$  to 500 and  $\text{R}=\text{H}$  or alkyl, is used as the starting material.

16. A process according to any one of claims 5 to 14, wherein a polyester formed from a dicarboxylic acid and a diol is used as the starting material.

17. A process for the preparation of the modified polymers claimed in any one of claims 1 to 4, wherein ethylene imine or an ethylene imine substituted amine or alcohol is reacted with a starting material of a polyester or polyether containing within the chain or attached thereto groups which will react directly with the ethylene imine compound.

18. A process according to claim 17, wherein the starting material is a polyester in which at least part of the acid residues are derived from an  $\alpha,\beta$ -unsaturated dicarboxylic acid or a halogen-substituted dicarboxylic acid.

19. A process according to claim 17, wherein the starting material is a polyether which contains  $\alpha,\beta$ -unsaturated carboxylic acid residues or side chains of the formula  $-(\text{CH}_2)_n-\text{Hal}$ , where Hal is chlorine or bromine and  $n=1.4$ .

20. A process according to any one of claims 8 to 19, wherein the ethylene imine containing reactant is an amine of the formula:



or



and R is a hydrogen atom or an alkyl group.

21. A process according to claim 20, wherein the ethylene imine containing reactant is 2-ethyleneimino-ethylamine, 3-ethylene-imino-propylamine, 3-ethyleneimino-butylamine, 5-ethyleneimino-pentylamine, 7-ethyleneimino-heptylamine or 3-ethyleneimino-propanol-1.

22. A process for the preparation of the modified polymers claimed in any one of claims 1 to 4, substantially as hereinbefore described.

23. A process for the preparation of the modified polymers claimed in any one of claims 1 to 4, substantially as described in any one of the foregoing Examples.

24. A modified polymer as claimed in any one of claims 1 to 4 when prepared by a process according to any of claims 5 to 23.

5 25. A process for the preparation of synthetic elastomers, which comprises crosslinking a predominantly linear polyester, polyether or polythioether which contains on average more than one ethylene imine group per molecule, and which has a mean molecular weight of at  
10 least 1,000 and an ethylene imine equivalent of at least 500.

15 26. A process for the preparation of synthetic elastomers which comprises crosslinking a modified polymer claimed in any one of claims 1 to 4 and 24 by means of a crosslinking agent.

20 27. A process according to claim 26, wherein the crosslinking agent is a sulphonic acid alkyl ester, a dialkyl sulphate, an aryl sulphonic acid methyl ester having a negative substituent in the benzene ring, or a Lewis acid.

28. A process according to claims 25, 26 or 27, wherein the proportion of crosslinking agent is 0.2 to 10% by weight.

25 29. A process according to any one of claims 25 to 28, wherein the modified polymer is mixed with 0.2 to 3% of the crosslinking agent at room temperature and subsequently heated to a temperature of 50° C. to 100° C. to  
30 crosslink the polymers.

30 30. A process for the preparation of synthetic elastomers according to claim 25, substantially as hereinbefore described.

35 31. Synthetic elastomers when obtained by a process according to any one of claims 25 to 30.

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